

BNL- 71444-2003-IR
Informal Report

Low Cost Bioheating Oil Application

C.R. Krishna

May 2003

**Report on work done for the
NOCO Energy Corp.,
Tonowanda, NY 14150**

**Energy Sciences and Technology Department
Energy Resources Division
Brookhaven National Laboratory
Brookhaven Science Associates
Upton, New York 11973-5000**

**Under Contract No. DE-AC02-98CH10886 with the
United States Department of Energy**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency, contractor or subcontractor thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency, contractor, or subcontractor thereof.

Executive Summary

The report describes primarily the results of combustion tests carried out with a soy methyl ester (SME) that can be considered as a biofuel that does not quite meet the ASTM D 6751-02 specifications for biodiesel. The tests were performed in a residential boiler and a commercial boiler. Blends of the SME in distillate fuel (home heating fuel or equivalently, ASTM # 2 fuel oil) were tested in both the boilers. Similar tests had been conducted in a previous project with ASTM biodiesel blends and hence provided a comparison. Blends of the SME in ASTM # 6 oil (residual oil) were also tested in the commercial boiler using a different burner. Physical properties of the blends (in both the petroleum based fuels) were also measured. It was found that the SME blends in the distillate burned, not surprisingly, similarly to biodiesel blends. Reductions in NO_x with blending of the SME were the most significant finding as before with biodiesel blends. The blends in # 6 oil also showed reductions in NO_x in the commercial boiler combustion tests, though levels with # 6 blends are higher than with # 2 blends as expected. A significant conclusion from the physical property tests was that even the blending of 10% SME with the # 6 oil caused a significant reduction in viscosity, which suggests a potential direction of application of such blends.

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	iii
1. INTRODUCTION.....	1
2. EXPERIMENTAL DETAILS.....	1
2.1 EXPERIMENTAL PLAN.....	1
2.2 DETAILS OF EXPERIMENTS WITH SOY METHYL ESTER BLENDS IN #2 FUEL OIL.....	3
2.2.1 PROPERTIES OF SOY METHYL ESTER (SME) BLENDS.....	3
2.2.2 EXPERIMENTS IN RESIDENTIAL BOILER.....	7
2.3 EXPERIMENTS IN COMMERCIAL BOILER.....	12
3.0 TESTS WITH RESIDUAL FUEL BLENDS.....	15
3.1 PROPERTIES OF RESIDUAL FUEL BLENDS.....	15
3.2 TESTS OF THE BLENDS IN THE COMMERCIAL BOILER....	18
4.0 CONCLUSIONS.....	19
5.0 ACKNOWLEDGEMENT.....	20
6.0 REFERENCES.....	20

FIGURES

Figure 1. Sulfur Content of SME-#2 fuel blends.....	4
Figure 2. Viscosity of SME and biodiesel blends.....	5
Figure 3. Cloud and pour point temperatures for the SME blends....	6
Figure 4. Cloud points for SME and biodiesel blends compared.....	6
Figure 5. Flash point temperatures for SME and biodiesel blends....	7
Figure 6. Residential boiler test set up.....	8
Figure 7. Carbon monoxide against excess air for SME blends.....	9
Figure 8. Carbon monoxide levels compared for SME and biodiesel..	10
Figure 9. NOx in the stack for SME blends.....	11
Figure 10. NOx from SME and biodiesel blends compared.....	12
Figure 11. Commercial boiler test set up.....	13
Figure 12. NOx emission in the commercial boiler with pressure atomizer.....	14
Figure 13. NOx in commercial boiler with pressure atomizer compared.....	15
Figure 14. Viscosities of SME- residual oil blends.....	16
Figure 15. Viscosities of SME- # 6 oil blends at two temperatures.....	17
Figure 16. Flash points of SME- # 6 oil blends.....	17
Figure 17. Air atomizing Burner set up.....	18
Figure 18. NOx levels for SME blends in residual oil with air atomized burner.....	19
Table 1. Fuel Analyses.....	3

1. Introduction

Biodiesel is a product that was developed over years as a fuel, to replace or blend with, petroleum diesel. The intended use is in diesel engines. This is reflected in the standard that has been approved by the American Society of Testing Materials (ASTM) as D6751-02 titled "Standard Specification for BIODIESEL Fuel (B100) Blend Stock for Distillate Fuels", which includes a requirement for a cetane number among other requirements. Biodiesel had been proposed for use as a blend with home heating oil, which was very similar in most properties to transportation diesel, by Brookhaven National Laboratory (BNL). Under the sponsorship of the Department of Energy, through the National Renewable Energy Laboratory (NREL), laboratory tests had been carried out which demonstrated the feasibility of such use without alteration to the conventional heating equipment in homes [1]. A field test in about 100 homes by an upstate fuel oil dealer has also been successfully conducted over the last heating season and is continuing during the current season [2] under the sponsorship of the New York State Energy Research and Development Authority (NYSERDA). There are increasing numbers of biodiesel producers and potential users.

One of the difficulties in the path of expanding use of biodiesel is its cost at present, which is higher than that for petroleum diesel. However, biodiesel has been tailored as a replacement for diesel and it was suggested that for continuous combustion applications, such as boilers and turbines, one might be able to relax the ASTM specifications in requirements such as acid content, cetane number, flash point and glycerine content. Such a product could be cheaper potentially and hence could find more acceptance for use as a boiler fuel. It could be used as a blend, therefore, with not only distillate fuels but also residual fuels. NYSERDA decided to support the investigation of this approach under the aegis of NOCO Energy Corporation, with the laboratory work to be performed at BNL. Such non-spec fuel was supplied by Archer Daniels Midland (ADM) Company. This report describes the work performed in the laboratory at BNL.

2. Experimental Details

The experiments were carried out essentially to the plan given below. Some of the relevant properties of the fuel obtained from ADM, which will be called hereafter Soy Methyl Ester (SME) as designated by ADM, were measured in the test laboratory at NOCO. The combustion experiments were carried out in a residential boiler and in a commercial boiler in the laboratories of the Energy Resources Division of BNL.

2.1 Experimental plan

The following tasks constituted the experimental plan, the first three of which are similar to those used in the biodiesel project previously [1]. The tasks with the residual fuel blends were developed for the present project. These tasks were supplemented by tasks labeled A4 and A7 to utilize the biodiesel data to evaluate the data obtained here and to complete this report. In addition, preliminary to the combustion tests, some of the fuel properties that are significant to burning in boilers were measured and will also be discussed below.

Task A1: Measure ignition performance.

Ignition tests will be conducted, on the chosen blend(s) with ASTM No.2 oil, by starting with a cold boiler (ambient conditions) and with a warm boiler. Measurements of smoke and carbon monoxide will be made during the ignition transient to the steady state. Control tests will be carried out with the base No.2 oil to measure change in performance.

Task A2: Measure steady state performance in a residential Boiler.

The steady state performance will be assessed by measuring stack emissions of carbon monoxide, carbon dioxide, smoke, and NO_x, as a function of excess air or stack oxygen. The performance of the cad cell will be checked to estimate reliability of the safety control system.

Task A3: Measure steady state performance in a commercial boiler.

The steady state performance will be assessed by measuring stack emissions of carbon monoxide, carbon dioxide, smoke, and NO_x, as a function of excess air or stack oxygen. A 2 million Btu per hour firing rate commercial boiler will be used for these tests.

Task A5: Develop bioheating oil blends with residual oil.

Properties of the bioheating oils and of residual oils will be used to develop appropriate blends for use in stationary boilers currently firing residual oils. At least one blend that would have properties similar to No. 4 oil will be prepared. Blend properties will be measured.

Task A6: Test residual oil blend.

The commercial Boiler facility at BNL will be used to test the blend 'equivalent' to No. 4 oil under steady state conditions. Smoke and gas measurements in the stack will be carried out.

Task A4: Compare biodiesel and bioheating oil performance.

The results from the above tasks will be compared with similar results from previous work done with biodiesel. From this, recommendations will be developed for further utilization of bioheating oils.

Task A7: Prepare a report.

A final report of the year's work will be prepared. This will also include recommendations for phase 2 of the project, during which the field tests will be completed.

2.2 Details of experiments with soy methyl ester blends in #2 fuel oil

2.2.1 Properties of soy methyl ester (SME) blends

The SME tested in this project was obtained from ADM, who also furnished the analysis given in Table 1 below along with that for heating oil to ASTM #2 specification.

Table 1. Fuel Analyses

Ultimate	SME	#2 Fuel
% Carbon	77.09	87.3
% Hydrogen	12.35	12.5
% Nitrogen	<0.01	0.021
% Sulfur	0.01	0.21
% Oxygen	≤10.52	--
HHV, Btu/lb	17100	18990

The most obvious differences (as with biodiesel) are in the oxygen content, the sulfur content and the heating value. Clearly, the sulfur value is comparable to that for a very low sulfur diesel.

Samples of blends of the SME in the heating oil were prepared and sent to NOCO Energy Corp.'s test laboratory. The sample blends were of 10%, 20% and 50% by volume of SME and were mixed well prior to dispatch. There were no apparent miscibility problems and this is consistent with what had been observed previously with biodiesel. It should be noted that the mixing was done at room temperature and the samples were transported at a time of the year when ambient temperatures were typical of early spring. Samples of neat SME and #2 fuel oil were also tested for the same properties. The properties measured were the flash point (Pensky-Martens), the kinematic viscosity, the cloud and pour points and also the sulfur content.

Figure 1 below gives the measured sulfur content in the blends. Within the limits of measurement, the value for the SME is zero and the trend is linear as expected for this additive defined chemical characteristic.

Sulfur content

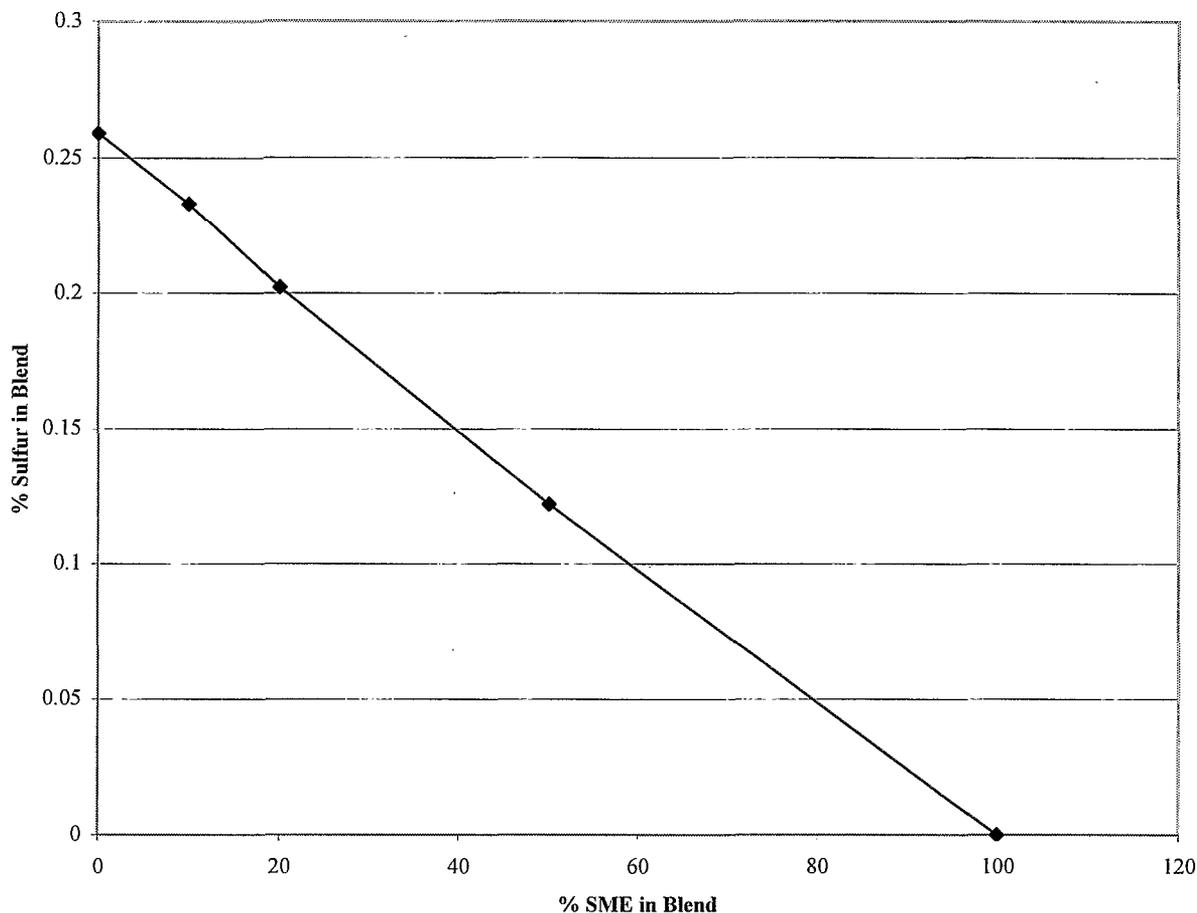


Figure 1. Sulfur Content of SME-#2 fuel blends

Figure 2 gives the viscosity as a function of the SME blend and compares the values reported in reference 1 for biodiesel blends. The two blends show similar trends, not quite linear, but the viscosity values for the SME blends are higher. The value for the No.2 fuel used to make the SME blends is also higher, though within the ASTM specification limits. This may be due the two fuel samples being different and also due to measurements at different laboratories. The difference in viscosity is not considered significant for the purposes of these evaluations.

Viscosity

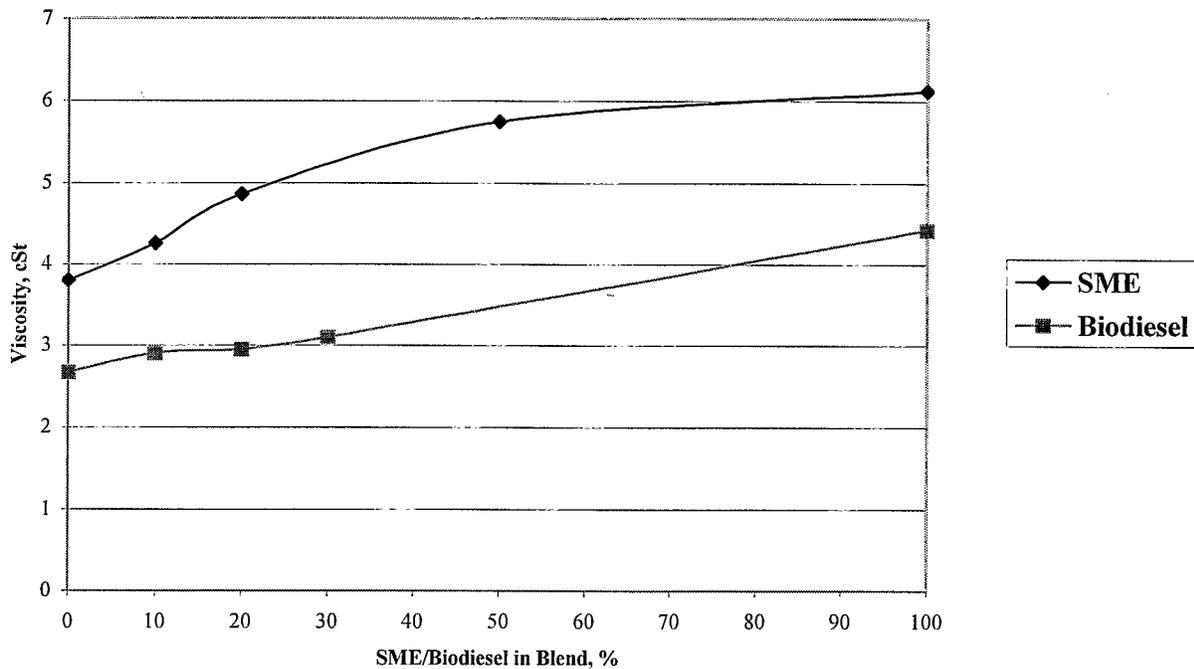


Figure 2. Viscosity of SME and biodiesel blends

The cold flow properties of biofuel blends are important from the storage, handling and flow points of view. The SME blend cloud and pour point temperatures were measured in a test laboratory and are given in figure 3. Both increase in a more or less parallel and linear fashion with increasing fraction of the soy methyl ester in the blend. Figure 4 compares the pour points for SME and biodiesel blends. It seems that the difference between the biodiesel and the SME blends is due to the difference in the values for the #2 fuel. As pour points had not been measured for the biodiesel, they could not be compared, but taken together, figures 3 and 4 suggest that the comparison would be similar.

Cloud and Pour Points

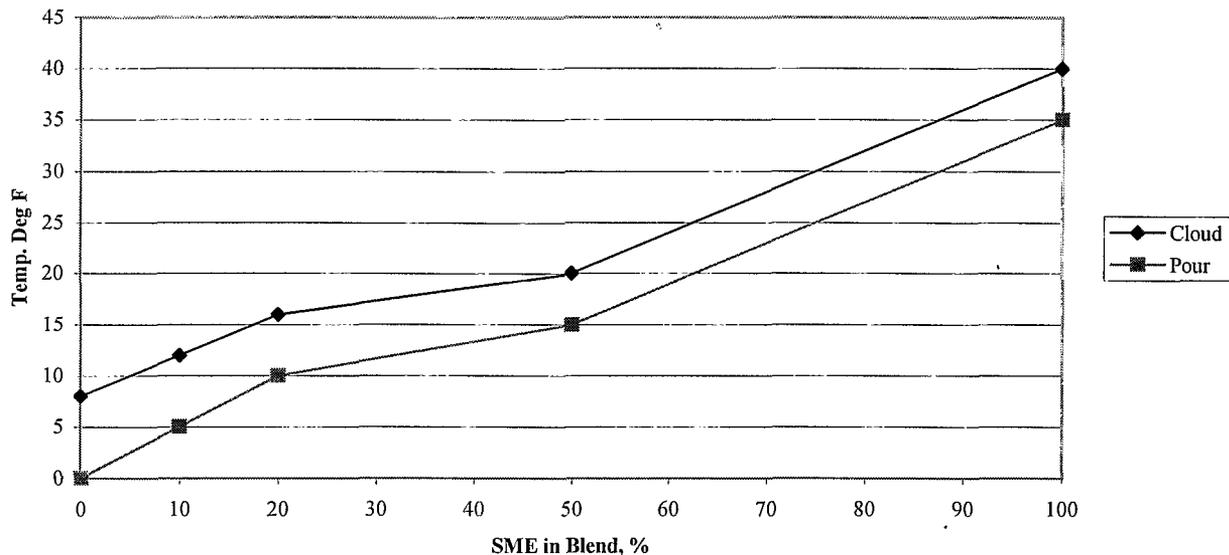


Figure 3. Cloud and pour point temperatures for the SME blends

Pour Points

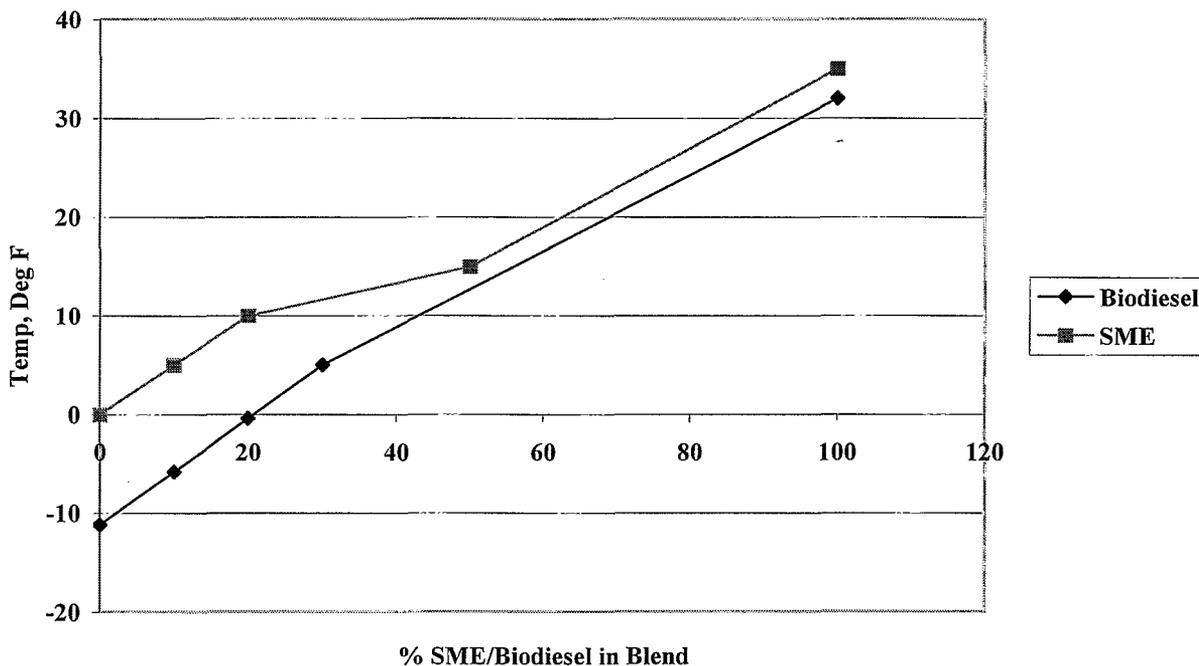


Figure 4. Cloud points for SME and biodiesel blends compared

Figure 5 below plots the measured flash points for the soy methyl ester blends and compares those for the biodiesel blends. It can be seen that the values and the trend up to the 50% blends are the same. Two values for the 100 % SME are plotted. The lower value was measured in the test laboratory with the other blends and the higher value was that in the specification sheet from ADM. One would have expected this value also to be close to the biodiesel value. Clearly, the ADM value seems too high, as it may even be

more than the end point for distillation. The measured value seems too low and might represent a measurement error or sample contamination. However, for the present purposes rectification of the discrepancy was not deemed critical. Blend evaluations have been performed assuming that the biodiesel and SME blends behave similarly with respect to flash point.

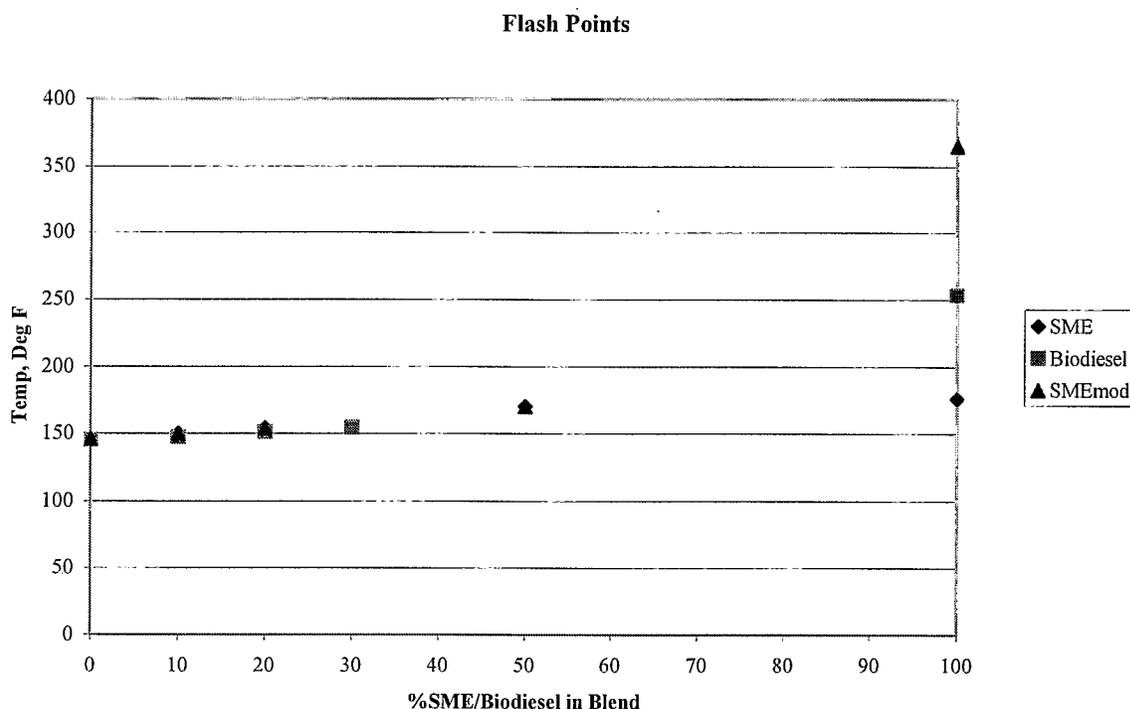


Figure 5. Flash point temperatures for SME and biodiesel blends

2.2.2 Experiments in residential boiler

The initial combustion experiments were conducted in the same residential boiler in which the biodiesel experiments had been conducted earlier. From the results of the comparison of the properties with biodiesel blends presented above, it is clear that, in terms of the flash points and viscosities, two properties important to liquid spray combustion, there is no significant difference between the two. As such, we do not expect to see any significant differences in gross combustion properties, in the ignition transient and steady state modes, between SME and Biodiesel blends. This was observed qualitatively in the start up prior to steady state tests. Of course, this is not obvious for features such as NO_x production, which depends on the fuel nitrogen content (not measured in the tests here) and on the details of the combustion process. Hence, steady state tests were conducted with primary emphasis on such features, particularly as NO_x reductions had been observed in the prior biodiesel blend tests [1].

Figure 6 below is a photograph of the test set up. The boiler is on the left and the instrument rack is on the right with the sample conditioning system in the middle. Concentrations of Carbon monoxide, Oxygen and Nitrogen Oxides in the stack were measured. Smoke was measured using a hand operated pump drawing on to smoke spot paper as is commonly done.

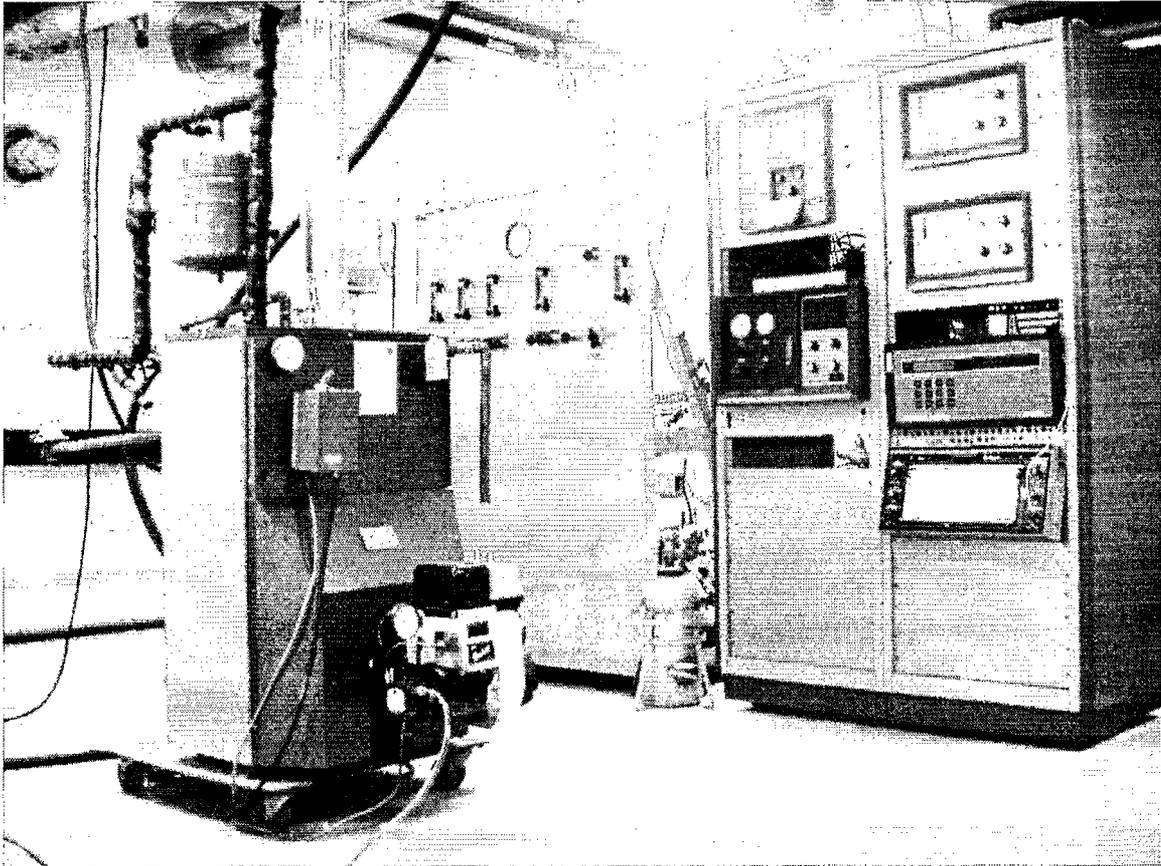


Figure 6. Residential boiler test set up

Figure 7 is a plot of the measured carbon monoxide levels in the stack against the excess air level as represented by the measured oxygen in the stack. The normal range of operation should be in a region of reasonably low carbon monoxide and the figure suggests that this range and the CO values are similar with SME blends to those with # 2 fuel oil. Of course, the CO levels increase outside this range and the smoke numbers also increase especially at the lower excess air levels.

Carbon Monoxide

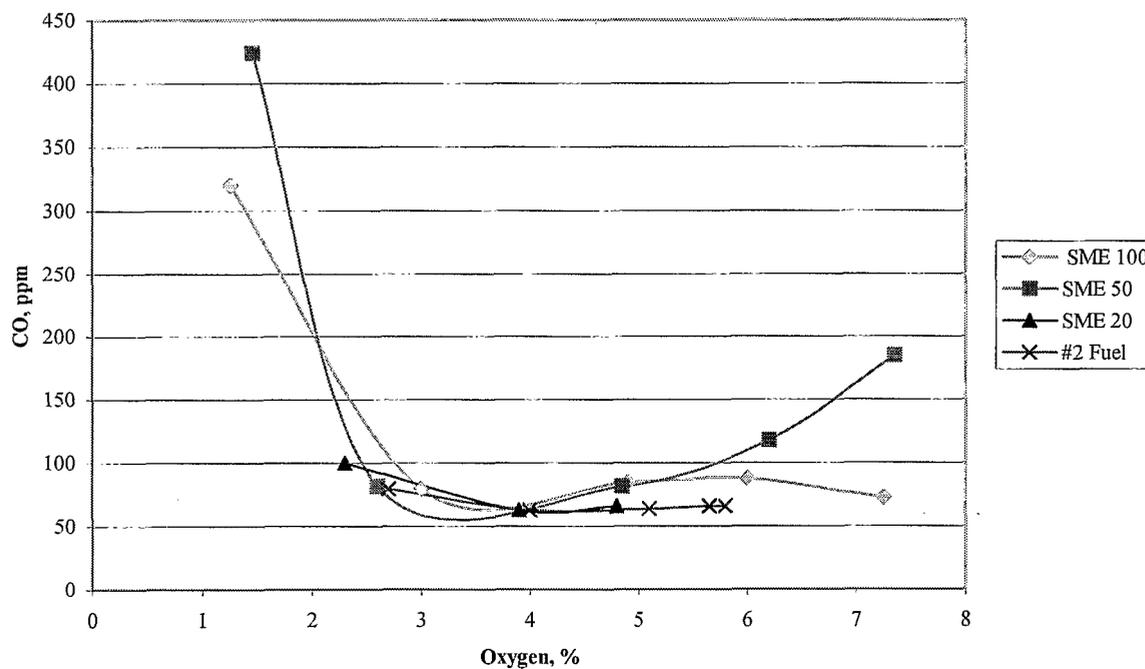


Figure 7. Carbon monoxide against excess air for SME blends

Figure 8 compares CO levels for the SME with those for Biodiesel. Within the normal operating range, it seems as though the levels for biodiesel are slightly lower. Much more careful and detailed measurements are needed before this observation can be established firmly and for the present, it would be more reasonable to say that the values are comparable. The extreme left point on the SME 100 curve was at too low an excess air and would not be a normal operating point with this burner and boiler combination.

CO vs O2 compared

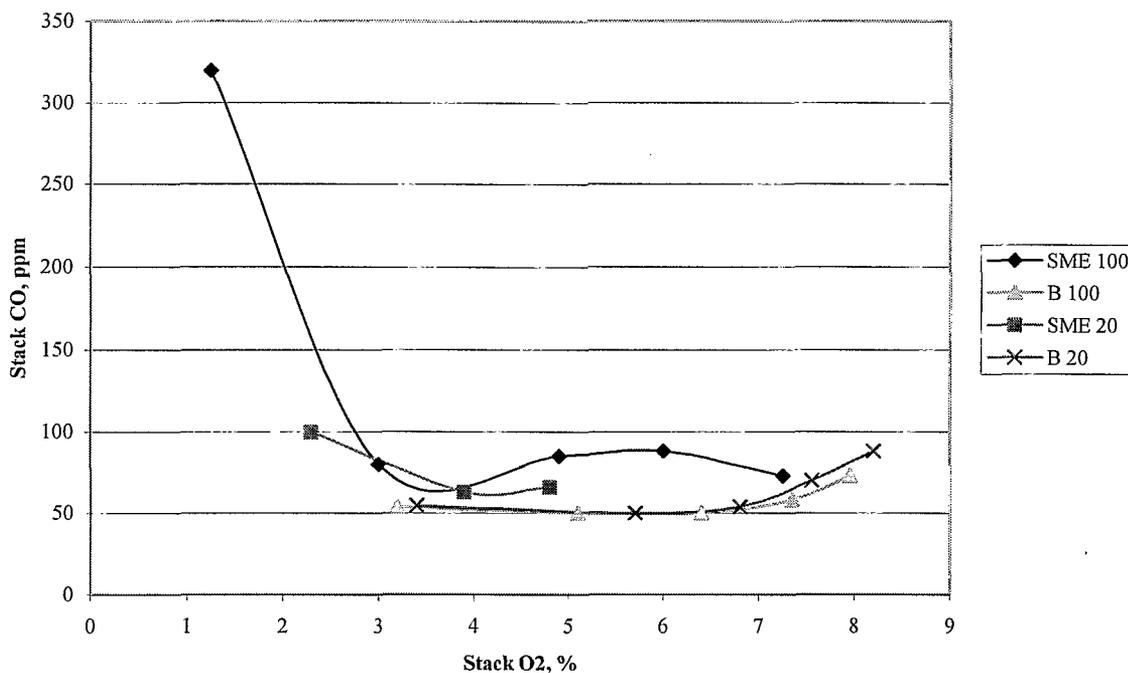


Figure 8. Carbon monoxide levels compared for SME and biodiesel

Figure 9 below compares the measured NOx values in the stack for all the SME blends tested, again as a function of excess air represented by the measured values of Oxygen in the stack. Broadly speaking, the NOx values reduce with the increase of the soy methyl ester in the blend, and with increasing excess air content. While the NOx values are higher for 100% SME than for 50% SME blend, the values are still less for these two blends than those for #2 fuel.

NOx in Residential Boiler

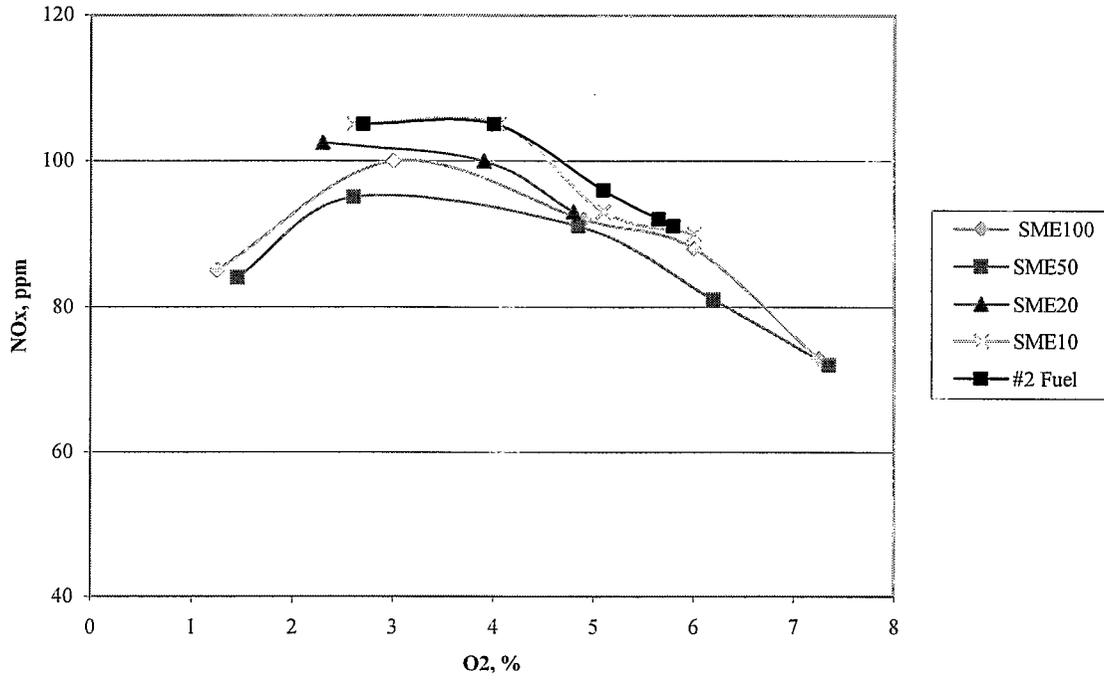


Figure 9. NOx in the stack for SME blends

Figure 10 compares NOx values for selected blends (for clarity) of SME and Biodiesel. The NOx reductions are higher with corresponding additions of SME compared to biodiesel. Whether other variables such as testing schedule, source materials, etc. have any bearing on this observation is not known.

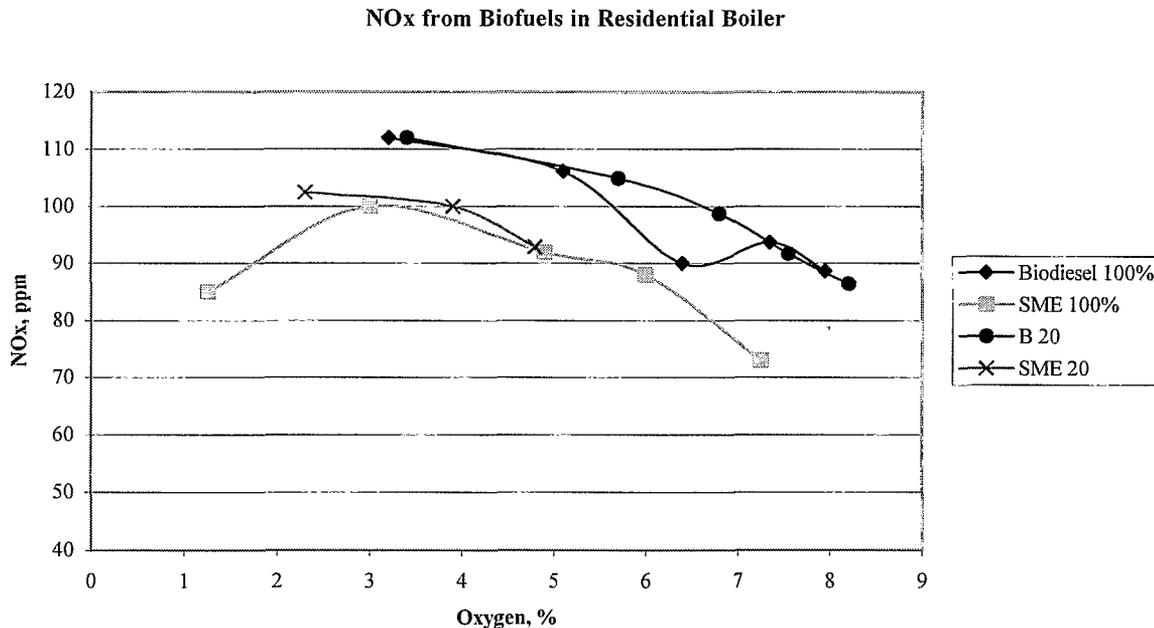


Figure 10. NOx from SME and biodiesel blends compared

2.3 Experiments in commercial boiler

The soy methyl ester blends were burned in the commercial boiler set up in the laboratory. Figure 11 is a photograph of the set up showing the burner and the fuel supply. The boiler is a commercial unit of 2 million Btu per hour firing capability. For these test, the boiler was operated under steaming conditions. The steam conditions were saturated at 15 psi and the steam was vented to the outside of the building. The burner is a standard commercial pressure atomized unit. The oil pressure was 150 psi. The blends were drawn from a plastic container on a scale (the container on the right in the picture), which was used to measure the fuel flow rate by timing. The large container on the right contains # 2 fuel oil, which is used to bring the system up to steady state before switching to the blend under test. The excess air was changed by the burner air setting. The temperature, smoke number, carbon monoxide, oxygen and NOx were measured in the stack with essentially the same instruments used in the residential boiler tests. The range of operating conditions was such that the smoke numbers remained between 0 and 1 and

the carbon monoxide concentrations were low and nearly constant. Hence, only the NO_x values will be reported here graphically and compared with the previous measurements for biodiesel blends.

Figure 12 shows the measured NO_x as a function of the excess air (again represented in terms of stack oxygen) for the SME blends tested. The first thing of note is that the NO_x levels are much lower than in the residential boiler case (Figure 9) suggesting that the flame is on the average 'less hot' in this boiler, if the Zeldovich mechanism holds good. Also, reduction in the NO_x levels are seen with addition of the soy methyl ester as before, but the percentage reductions are significantly higher for this case. Figure 13 compares the measured NO_x levels for a few blends of SME with the previous measurements for Biodiesel. In this case, while the additions of both biofuels reduce the NO_x levels, the reductions with addition of biodiesel are higher. Again, one should be cautious about drawing extended firm conclusions without much more experimentation to specifically understand these effects.

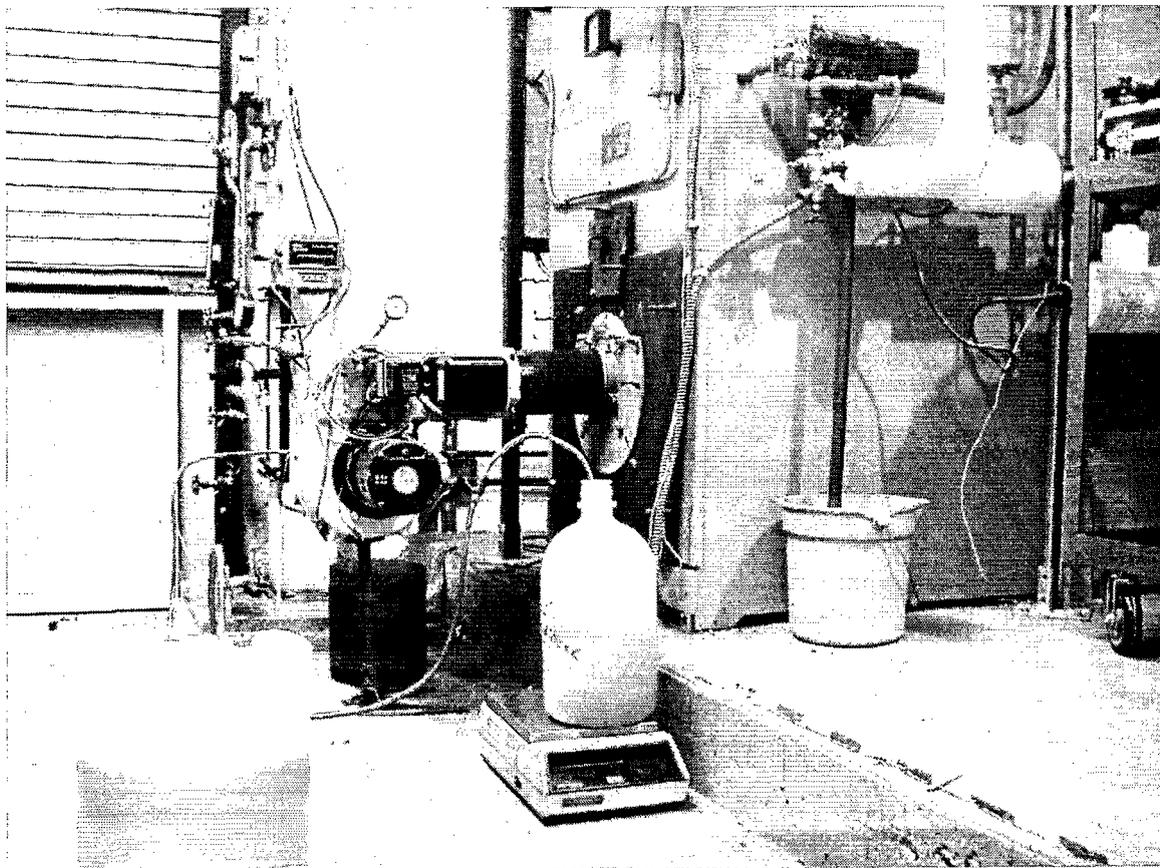


Figure 11. Commercial boiler test set up

NOx in Commercial Boiler for SME-#2 blends

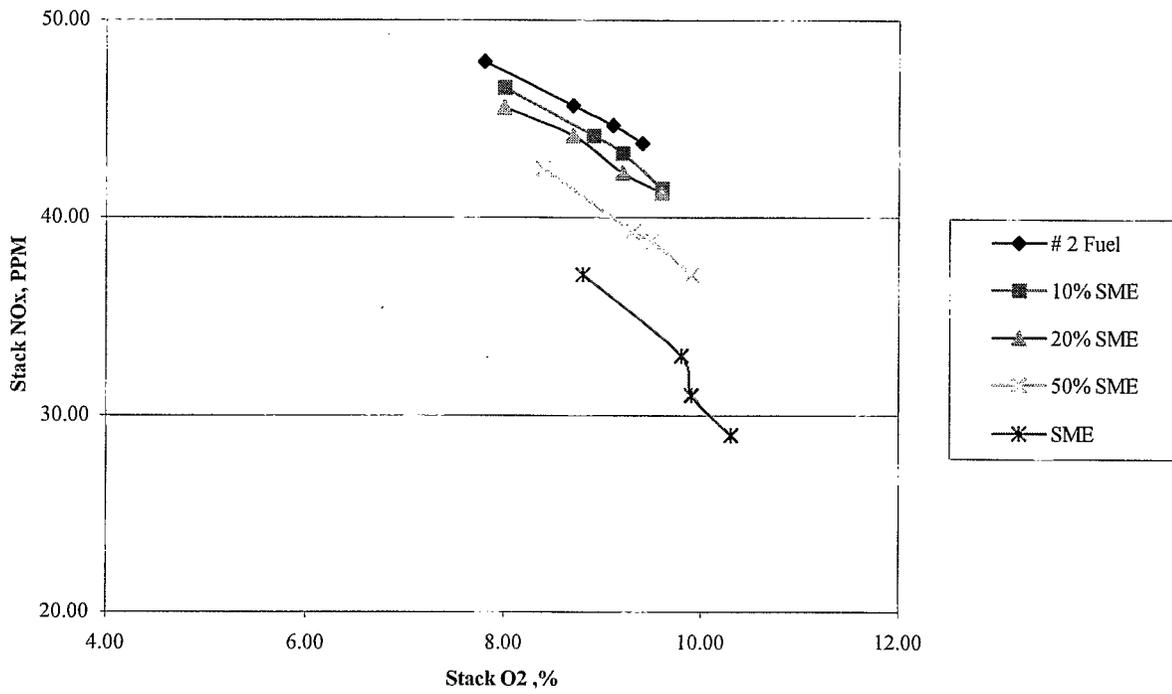


Figure 12. NOx emission in the commercial boiler with pressure atomizer

NOx in Commercial Boiler compared

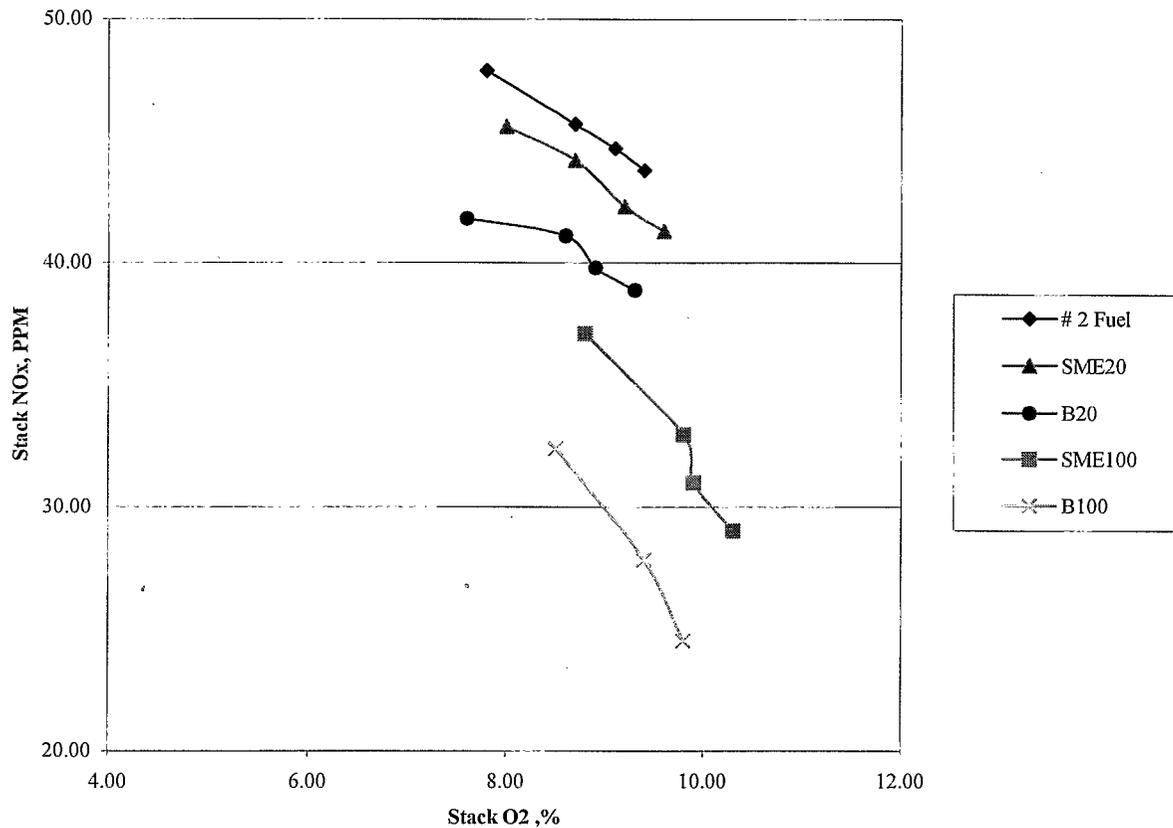


Figure 13. NOx in commercial boiler with pressure atomizer compared

3.0 Tests with Residual Fuel Blends

3.1 Properties of Residual Fuel blends

These were also measured at NOCO's test laboratory. Figures 14 and 15 give the viscosity measured at two different temperatures as a function of the percentage of the SME in the blend. The measurement at 'room temperature' of 78⁰ F was only at 50% and 100%. It is interesting to note that in the blends heated to 122⁰ F, even adding 10% biodiesel seems to offer a substantial reduction in viscosity from that for the residual oil. If valid, this suggests that small amounts of blending with SME can have a big impact on flow and atomization characteristics. The value at 78⁰ F at a blend of 50% (Figure 15) suggests that that flow qualities comparable to No. 4 oil could be achieved at similar blend ratios. The flash points of the blends are shown in figure 16. There was some confusion as to the value for this residual fuel sample and hence it is not included here. The soy methyl ester has a higher flash point than this sample of # 6 fuel oil and the change is more or less linear with blend percentage.

Viscosity of SME-No. 6 Blends

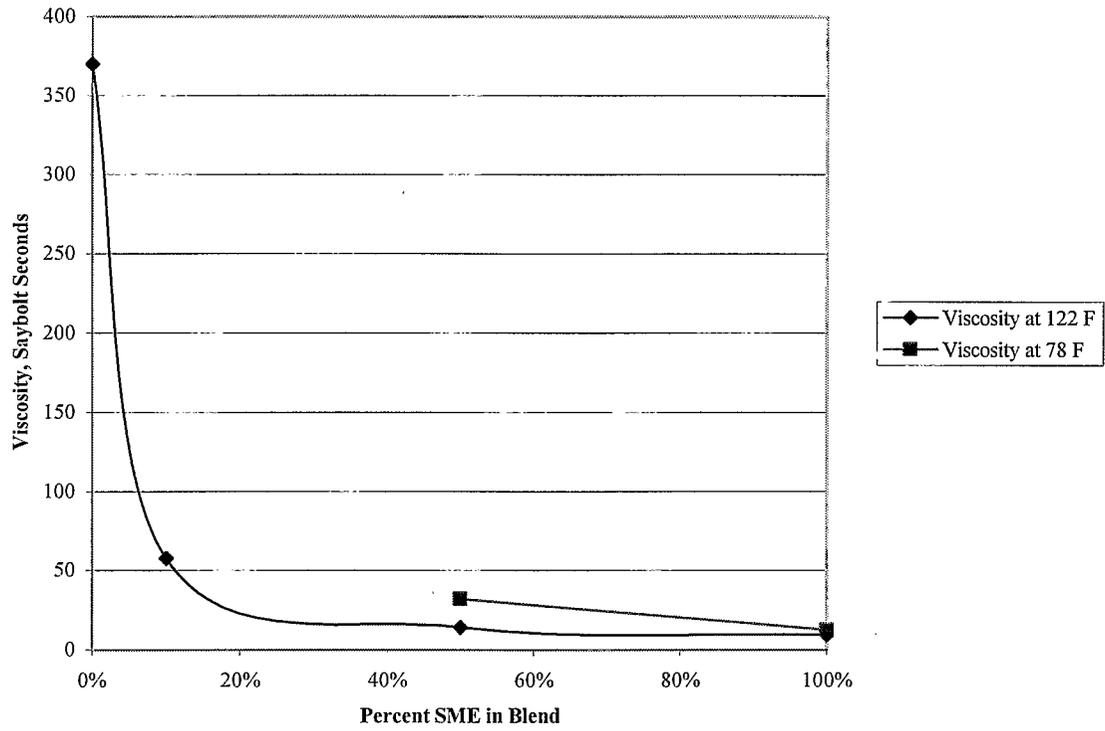


Figure 14. Viscosities of SME- residual oil blends

Viscosity of SME Blends (2)

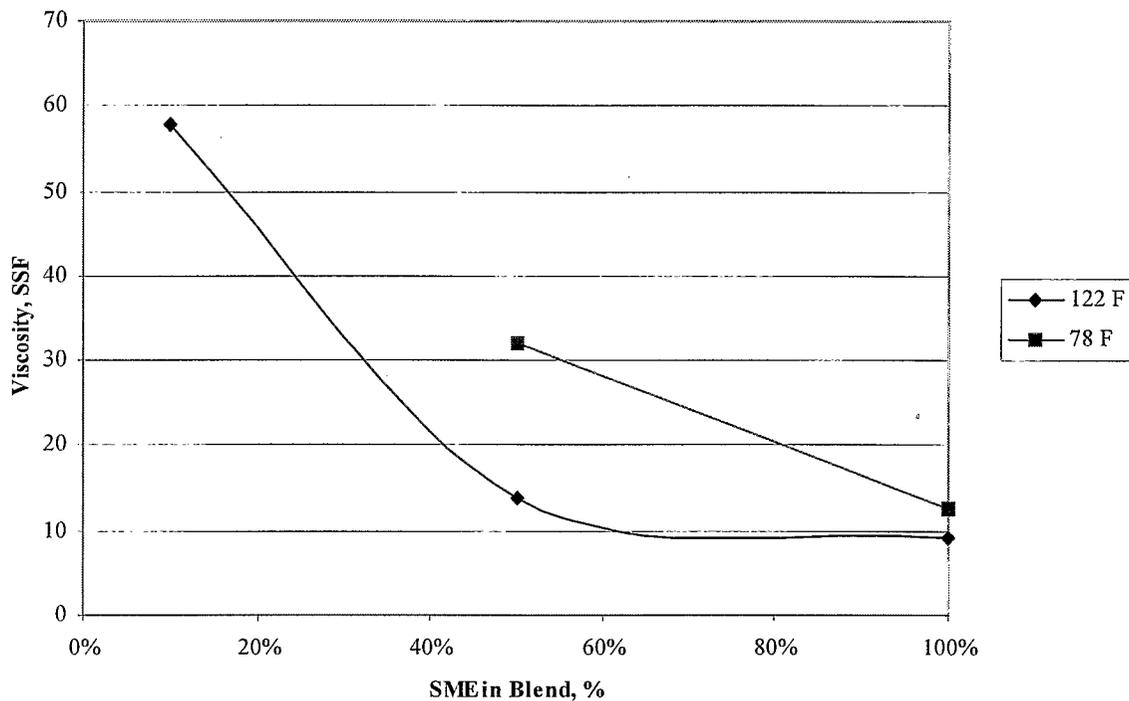


Figure 15. Viscosities of SME- # 6 oil blends at two temperatures

Flash Point of SME Blends in No. 6 oil

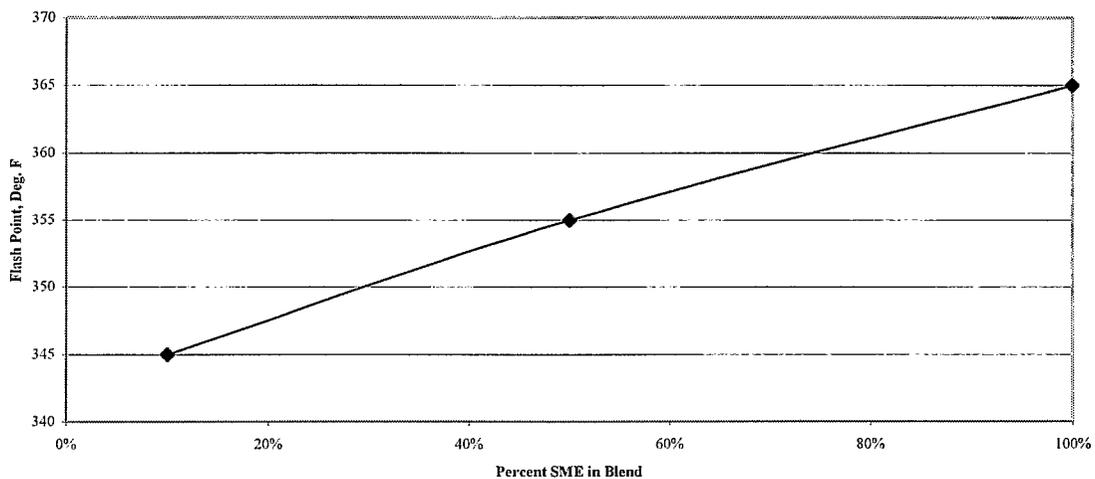


Figure 16. Flash points of SME- # 6 oil blends

3.2 Tests of the blends in the commercial boiler

The commercial boiler and its burner are meant to use distillate fuels to ASTM no. 2 specifications normally. The burner has a conventional pressure atomized nozzle and an oil pump and blower on the same motor drive shaft. There is no provision for fuel heating. This system cannot be used for burning fuels with characteristics similar to residual fuel. Consequently, the original set of tasks (see above), it had been proposed to develop a blend with high enough percentage of the soy methyl ester that will have viscosity characteristics similar to, at the worst, of ASTM no. 4 oil. It was planned to combust this using the commercial burner. Discussions during the course of the project altered the scope to include burning both the residual fuel and blends with lower percentages of the SME. Hence, the fuel system and burner had to be altered to make this feasible. There was available an external fuel system with a pump of much larger capacity than required by the firing rate, which had been used with a compressed air atomizer in the past. There was also provision for heating the fuel stored in a drum and for heating the lines going to the nozzle. A large part of the flow from the pump has to by-passed back to the drum storing the fuel. This system was modified with a calibrated orifice in the fuel line to the nozzle to regulate the flow. This was required as the nozzle is an internal mixing air atomizer and a delicate balance of the air and fuel pressures would otherwise be required to control the firing rate. The air for atomizing was supplied by a compressor. Figure 17 is a photograph of the set up.

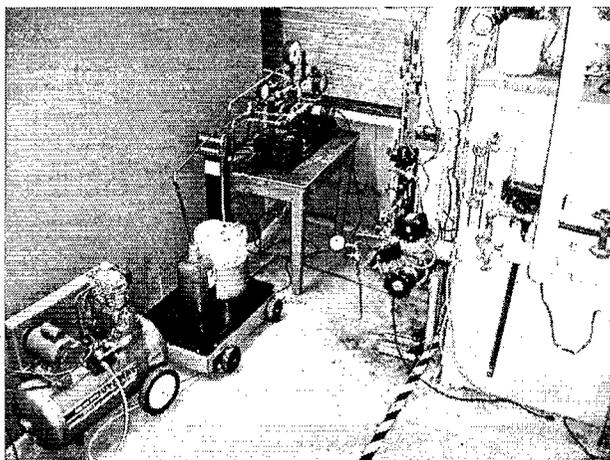


Figure 17. Air atomizing Burner set up

All of the results reported below for the residual fuel blends including the 100% SME (figure 18) were obtained using this modified air atomized burner. There were difficulties in handling the residual blends because of the need to heat the fuel drum and the lines. As before, the burner was started and the boiler brought to steady steaming conditions on distillate fuel. The fuel was switched to the blend under test and after steady flow

conditions were reached the measurements were made. Under the operating conditions that were achieved, the smoke and carbon monoxide levels in the stack for the residual fuel were higher than desired and higher than with the blends. As such, the comparison for the NOx emissions in figure 18 below is somewhat misleading. Assuming that lower smoke and carbon monoxide levels entail 'hotter' flames, it could be that reductions in NOx due to addition of the SME are even higher. It is conceivable that the nitrogen content of the residual fuel, which was not measured is high and is partly responsible for the high NOx levels as is also suggested by the much lower NOx levels for the 100% SME. The difference in the NOx levels for 100% SME shown by figure 13, which is from the commercial pressure atomized burner and figure 18, which is from the air atomized burner, is probably due to the differences in the combustion profiles (average flame temperatures) between the two burners.

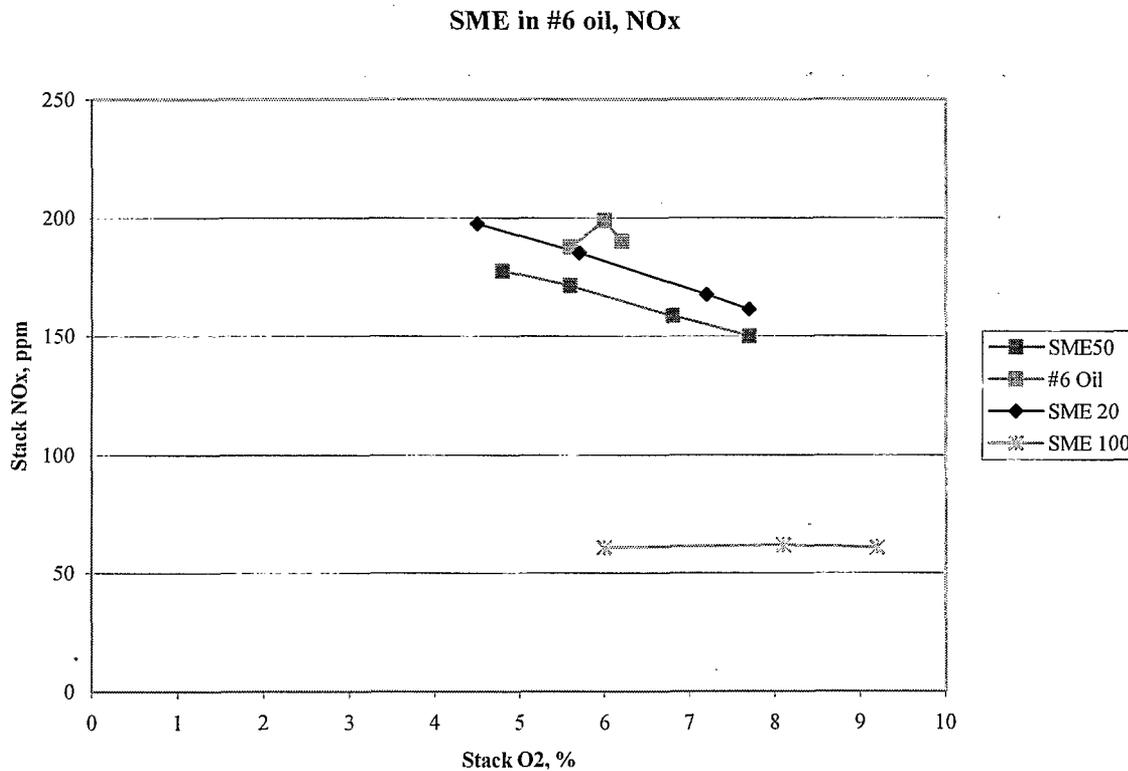


Figure 18. NOx levels for SME blends in residual oil with air atomized burner

4.0 Conclusions

The blending of the soy methyl ester with both distillate and residual fuels in the laboratory did not pose any problems. The combustion performance of the blends in home heating oil, as determined from the tests carried out in the laboratory, was similar

to that with biodiesel blends previously tested. This is the first time blends with residual oil had been tested and so no comparison with biodiesel is possible. SME blends in distillate oil showed reductions in NO_x levels as seen with biodiesel blends. Similarly, the reductions were more significant in the commercial boiler tests. The residual blends were of course combusted only in the commercial boiler and also showed significant reductions in NO_x emissions. The addition of only 10% of SME to this sample of residual fuel showed a significant reduction in viscosity and this might suggest an avenue of application for such blends.

Clearly, commercial use of blends with distillate fuel is still subject to caveats similar to those for biodiesel blends in terms of poorer cold flow properties, and also potential effects on non-metallic materials when used in existing equipment. Benefits of blending with residual fuels as shown here include significant reduction in viscosity, which could reduce or eliminate the need to heat the fuel for flow and reductions in NO_x and Sulfur dioxide.

5.0 Acknowledgement

Ray Albrecht, the program manager at NYSERDA, has been of invaluable help in his consistent encouragement and in technical discussions. Gary Roesch, until recently of NOCO, was a source of support and has been a pleasure to work with. Chris Bergstrom at NOCO's laboratory is owed thanks for providing excellent measurements of fuel properties. At BNL, the work could only have been accomplished with the excellent technical support in the laboratory of Yusuf Celebi and George Wei. Tom Butcher has been a source of support and engineering guidance. Roger McDonald's review helped to improve the writing of the report. Skip Hauth's review and comments helped to improve the final version. Thanks are due to NOCO and NYSERDA for the funding of the project, as well as DoE for co-funding. Thanks are due to Gerry Downing of Archer Daniels Midland Company for supplying the Soy methyl Ester, for data sheets on the material and for discussions.

6.0 References

1. C.R. Krishna, Biodiesel Blends in Space Heating Equipment, BNL Informal Report 68852, 2001.
2. C.R. Krishna, T.A. Butcher, R.J. McDonald, Y. Celebi and G. Wei, and Ralph R. Mills, Update on Use of Biodiesel Blends in Boilers, Paper no. 02-06, Proceedings of the 2002 National Oilheat Research Alliance Technology Symposium, BNL-52670, 2002.